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(54) Process for the separation of alkenes and alkanes

Verfahren zur Trennung von Alkenen und Alkanen

Procédé pour la séparation d'alcènes et d'alcanes

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(73) Proprietor: **THE BOC GROUP, INC.**
Murray Hill, New Providence, New Jersey
07974-2082 (US)

(72) Inventors:
• **Bülow, Martin**
Basking Ridge, New Jersey 07920 (US)
• **Guo, Chang J.**
Bridgewater, New Jersey 08807 (US)

- **Shen, Dongmin**
Chatham, New Jersey 07928 (US)
- **Fitch, Frank R.**
Bedminster, New Jersey 07928 (US)
- **Shirley, Arthur I.**
Piscataway, New Jersey 08854 (US)
- **Malik, Virginia A.**
Linden, New Jersey 07036 (US)

(74) Representative: **Wickham, Michael et al**
c/o Patent and Trademark Department The BOC
Group plc Chertsey Road
Windlesham Surrey GU20 6HJ (GB)

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Description

[0001] This invention relates to the separation of hydrocarbon gases, and more particularly to the separation of gaseous alkenes from alkanes by adsorption. Specifically, the invention relates to the separation of propene from propane or the separation of ethene from ethane by pressure swing adsorption (PSA) using a modified 4A zeolite adsorbent.

[0002] It is known to separate alkenes (e.g. propene) from alkanes (e.g. propane) by distillation. The propene-propane mixture is fed into a C₃-splitter, which typically is a 2-column distillation system. The second column is substantially equal in size to the first column. The first column separates a substantial portion of the propane to produce a chemical or refinery grade propene of at least 90 volume percent purity, typically about 96 volume percent. The second column improves the purity level to 99+ volume percent to obtain polymer grade propene. The separation of propene from propane by distillation is both difficult and costly because the process requires two large columns and is very energy intensive. It is also known to separate alkenes from alkanes by adsorption. US-A-4,917,711 describes the adsorption of an alkene from a mixture containing the alkene and an alkane using an adsorbent comprising a copper compound and a high surface area support such as silica gel or zeolite molecular sieves, such as 4A zeolite, 5A zeolite, type X zeolite or type Y zeolite.

[0003] East German (DD) Patent No. 150885 describes the separation of alkenes from alkanes using 4A zeolite which has some of its exchangeable cations replaced by calcium or magnesium ions.

[0004] US-A-5,365,011 describes the separation of alkenes having 2 to 6 carbon atoms from alkanes having 2 to 6 carbon atoms by pressure swing adsorption at temperatures in the range of about 50 to 200°C using 4A zeolite. The 4A zeolite may have up to 25% of its exchangeable sodium ions replaced by other ions, including potassium ions, calcium ions, strontium ions, etc., provided that the presence of the other ions does not cause the 4A character of the adsorbent to change.

[0005] Breck et al, "The Properties of a New Synthetic Zeolite, Type A", Journal of the American Chemical Society, Vol. 78, Number 23, 1956, pp. 5963-5977, describes the adsorption of various hydrocarbons using partially potassium-exchanged type 4A zeolite.

[0006] Because of the importance of adsorption as a method of separating alkenes from alkanes, adsorbents having enhanced alkene/alkane separation ability are continuously sought. This invention provides new adsorbents which can efficiently and effectively separate selected alkenes from selected alkanes.

[0007] According to the present invention there is provided a method of separating an alkene selected from ethene, propene, normal butene or mixtures of these from a gas mixture comprising said alkene and an alkane selected from ethane, propane, normal or branched chain butanes and mixtures of these by a pressure swing adsorption process comprising the steps:

(a) passing the gas mixture through at least one adsorption zone containing type A zeolite having, as its exchangeable cations, about 50 to about 85% sodium ions, about 15 to about 40% potassium ions and 0 to 10% other ions selected from Group IA ions other than sodium and potassium, Group IB, Group IIA ions, Group IIIA ions, Group IIIB ions, lanthanide series ions thereby adsorbing at least part of said alkene from said gas mixture and producing an alkene-depleted gas; and

(b) regenerating the zeolite, thereby producing an alkene-enriched gas.

[0008] Preferably, the adsorption step, i.e., step (a), is carried out at a pressure in the range of about 1 to about 120 bara, and step (b) is carried out at a pressure in the range of about 0.15 to about 5 bara. In a more preferred aspect, step (a) is carried out at a pressure in the range of about 1 to about 25 bara and step (b) is carried out at a pressure in the range of about 0.2 to about 2 bara.

[0009] The method of the invention is particularly useful for the separation of the alkenes from alkanes when the alkene and the alkane being separated contain the same number of carbon atoms.

[0010] The method of the invention is especially useful for separating ethene from gas mixtures containing alkanes, especially gas mixtures containing ethane, and it can be effectively used to separate ethene from a gas mixture when the gas mixture contains only ethene and ethane.

[0011] Preferably, step (a) comprises passing the gas mixture through the preferred zeolite of the first embodiment, i.e. type A zeolite having as its exchangeable cations, about 55 to about 80% sodium ions, about 20 to about 35% potassium ions and 0 to about 5% ions selected from said residual ions, and in a most preferred aspect of this preferred embodiment, step (a) comprises passing the gas mixture through type A zeolite whose exchangeable cations consist substantially of sodium and potassium ions.

[0012] The adsorbent may be at least partly regenerated by depressurising and preferably evacuating the adsorption zone. Additionally, or alternatively, the adsorbent can be at least partly regenerated by purging the adsorption zone

with alkene-depleted gas.

[0013] If desired, the adsorption zone may be purged with alkene-enriched gas prior to step (b).

[0014] Step (b) may be at least partly carried out by purging the adsorption zone with alkene-depleted gas.

[0015] If desired, the adsorption zone may be at least partially repressurised with alkene-depleted gas after step (b).

[0016] Alkenes which can be separated by the process of the invention are the normal alkenes having 2 to 4 carbon atoms, which include ethene, propene, butene-1 and butene-2. In a preferred embodiment, the process of the invention is applied to the separation of normal alkenes having 2 to 4 carbons from alkanes having 2 to 4 carbon atoms. The most beneficial application of the invention involves the separation of a normal alkene having 2 to 4 carbon atoms from the corresponding alkane, i.e., an alkane having the same number of carbon atoms as the alkene being separated.

Preferred separations include ethene-ethane separation, propene-propane separation and the separation of one or more normal or branched chain butanes. The most preferred separation is ethene-ethane separation.

[0017] The process of the invention can be carried out in a system comprising a single adsorption unit or a battery of adsorption units operated in phase, or a plurality of adsorption units or batteries of adsorption units operated out of phase, whichever is desired. When a system comprising a single adsorption unit or a battery of units all of which are operated in phase is used, the adsorption step must be periodically stopped to permit regeneration of the adsorbent bed(s), whereas when a plurality of adsorption units are employed in parallel and operated out of phase, one or more units can be in adsorption service adsorbing the desired gas component, while one or more other units are undergoing regeneration to desorb and collect the adsorbed gas component. Operation of the adsorption systems of the invention is cyclical. In the preferred adsorption process, cycles are repeatedly carried out in a manner such that production of the desired product gas is substantially continuous. In preferred embodiments of the invention, the process is carried out in a system comprising multivessel adsorption systems with the vessels arranged in parallel and operated out of phase, such that one vessel is in the adsorption phase while another is in the adsorbent regeneration phase, with each vessel being packed with the novel adsorbent of the invention.

[0018] The steps of the PSA process used in carrying out the alkene-alkane separation are not critical to the invention. In general, the adsorption cycle includes, as basic steps, an adsorption vessel pressurisation step, a production (adsorption) step and an adsorption regeneration step. During the vessel pressurisation step, the pressure in the adsorption vessel in which the adsorption process is carried out is raised to the desired adsorption pressure. During the production step, a gaseous alkene and alkane-containing feed is passed cocurrently through the adsorption vessel (in the direction from the feed inlet end towards the non-adsorbed product outlet) at the desired adsorption pressure. As the feed gas passes through the adsorption vessel, an alkene-enriched component is adsorbed and an alkene-depleted non-adsorbed gas fraction passes out of the adsorption vessel. The bed regeneration step is carried out by countercurrently (in the direction opposite the cocurrent direction) reducing the pressure in the adsorption vessel and/or evacuating the vessel with a vacuum pump or other evacuation means, thereby desorbing the alkene-enriched product gas from the vessel. The PSA cycle used in the invention may include steps other than the basic steps described above. For example, the cycle may include one or more bed equalisation steps, a non-adsorbed product backfill step, a countercurrent non-adsorbed product purge step and a cocurrent desorbed product gas purge step at or below the desired adsorption pressure. The cocurrent purge generally precedes the evacuation step, and is generally carried out after any cocurrent depressurisation steps, e.g. equalisation steps. Countercurrent purge is generally carried out during or after countercurrent evacuation of the adsorption vessel. The sequential order and duration of the various steps are not critical, and these may be varied, as desired.

[0019] The adsorbents used in the invention are sodium and potassium-exchanged type A adsorbents about 50 to 85% of whose exchangeable cation sites are occupied by sodium ions, about 15 to 40% of whose exchangeable cation sites are occupied by potassium ions and optionally up to about 10% of whose exchangeable cation sites are occupied by ions other than sodium and potassium ions. In preferred embodiments when ions other than sodium and potassium ions are present, they do not occupy more than about 5% of the total exchangeable cation sites.

[0020] Such other ions include Group IA ions other than sodium and potassium, e.g. lithium ions, Group IB ions, e.g. copper I ions, silver I ions, etc., Group IIA ions, e.g. calcium ions, magnesium ions, strontium ions, etc., Group IIIA ions, e.g. aluminium ions, Group IIIB ions, e.g. gallium ions, and ions of the lanthanide series of elements. Preferred adsorbents are type A zeolites whose exchangeable cation sites are occupied substantially by sodium ions and potassium ions. Preferred type A zeolites have substantially only sodium and potassium ions as exchangeable cations, and about 60 to 85% of their exchangeable cation sites are occupied by sodium ions and about 15 to about 40% of its sites are occupied by potassium ions, and most preferred adsorbents are type A zeolites having substantially only sodium and potassium ions as exchangeable cations and about 65 to 80% of whose sites are occupied by sodium ions and about 20 to 35% of whose sites are occupied by potassium ions.

[0021] The temperature at which the adsorption step of the PSA process is carried out depends upon a number of factors, such as the particular alkene and alkane being separated, the particular adsorbent being used and the pressure at which the adsorption step is carried out. In general, the adsorption step is carried out at a minimum temperature of about 50°C, and it is preferably carried out at a minimum temperature of about 70°C. The upper temperature at which

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the adsorption step of the process is carried out is a matter of choice. In general, the adsorption step can be carried out at a temperature below the temperature at which the alkene being separated undergoes chemical reaction, e.g. oligomerisation or polymerisation. In general, the adsorption step of the process can be carried out at temperatures up to about 200°C, but in preferred embodiments the upper adsorption temperature does not exceed about 175°C, and in most preferred embodiments, it does not exceed about 160°C.

[0022] The pressures at which the adsorption and adsorbent regeneration steps are carried out are likewise a matter of choice, and in general, these steps can be carried out at any of the usual pressures employed for gas PSA processes. The pressure at which the adsorption step is carried out is determined by economics.

[0023] Typically, the adsorption step is carried out at pressures in the range of about 0.5 to about 50 bara (bar absolute), and this step is preferably carried out at pressures in the range of about 1 to about 25 bara; and typically, the adsorbent regeneration step is carried out at pressures in the range of about 1.5 to about 5 bara and this step is preferably carried out at pressures in the range of about 0.2 to about 2 bara.

[0024] It will be appreciated that it is within the scope of the present invention to utilise conventional equipment to monitor and automatically regulate the flow of gases within the system so that it can be fully automated to run continuously in an efficient manner. The invention is further illustrated by the following examples in which, unless otherwise indicated, parts, percentages and ratios are on a volume basis.

EXAMPLES 1-3

[0025] These examples were carried out in a laboratory pressure swing adsorption apparatus comprising a pair of parallel-arranged stainless steel adsorption vessels, each having a volume of about 0.77 litres and each being packed with about 1185-1235 grams of the indicated zeolite. Each vessel was equipped with an external heater. The adsorption cycle consisted of the steps: bed equalisation (pressurisation) (2 secs), cocurrent pressurisation with feed gas (8 secs), cocurrent adsorption of the feed gas (50 secs), bed equalisation (depressurisation) (2 secs) and countercurrent depressurisation (58 secs). The total time for a half-cycle was 60 secs. Each experiment was carried out for a minimum period of twelve hours, which ensured steady state conditions. The adsorption step was carried out at a pressure of about 5 bara, the beds were equalised to a pressure of about 3 bara, and the beds were countercurrently depressurised to a pressure of about 1.3 bara. A feed gas composed of about 50% ethene and about 50% ethane (by volume) was used as the feed gas. The flow rate of the feed stream, high pressure product (HPP) and low pressure product (LPP), which are determined for standard conditions, i.e., room temperature and atmospheric pressure are reported in standard litres per minute (SLPM). The results are reported in the Table.

[0026] Adsorbent A is zeolite A substantially all of whose exchangeable cations are sodium ions; adsorbent B is zeolite A having as exchangeable cations 79.4% sodium ions and 20.6% potassium ions; and adsorbent C is zeolite A having as exchangeable cations 76.4% sodium ions and 23.7% potassium ions. The reported temperatures are average temperatures in the vessels throughout the entire cycle.

EXAMPLE 4

[0027] The procedure of Example 3 was repeated, except that the adsorption cycle step durations were: bed equalisation (4 secs), cocurrent pressurisation with feed gas (8 secs), cocurrent adsorption of the feed gas (108 secs), bed equalisation (2 secs) and countercurrent depressurisation (116 secs). The total time for a half-cycle was 120 secs. The results are reported in the Table.

EXAMPLE 5

[0028] The procedure of Example 4 was repeated except that the feed gas comprised 77.5% ethene and 22.5% ethane and the adsorption cycle step durations were: bed equalisation (8 secs), cocurrent pressurisation with feed gas (8 secs), cocurrent adsorption of the feed gas (110 secs), bed equalisation (4 secs) and countercurrent depressurisation (116 secs). The total time for a half-cycle was 120 secs. The results are reported in the Table.

TABLE

Flow Rate, SLPM (standard litres per minute)							
Example	Adsorbent	Adsorption Temp, °C	Feed	HPP	LPP	Ethene Recovered, %	Ethane Rejected, %
1	A	117	5.92	1.08	4.84	92.27	28.68
2	B	120	5.50	1.10	4.40	94.04	34.05

TABLE (continued)

Flow Rate, SLPM (standard litres per minute)							
Example	Adsorbent	Adsorption Temp, °C	Feed	HPP	LPP	Ethene Recovered, %	Ethane Rejected, %
3	C	144	4.17	1.07	3.10	92.59	42.00
4	C	162	2.92	0.75	2.18	93.31	42.75
5	C	149	2.93	0.43	2.49	94.26	46.91
HPP= High pressure product; LPP= Low pressure product							

[0029] Example 1 is a comparative example and Examples 2-5 are within the scope of the invention. A comparison of the results of the examples illustrates that partially potassium-exchanged zeolite A (Examples 2-5) provides significantly better ethene recovery and ethane rejection than does the base zeolite A, a substantially 100% sodium-exchanged zeolite (Example 1).

Claims

1. A method of separating an alkene selected from ethene, propene, normal butenes or mixtures of these from a gas mixture comprising said alkene and an alkane selected from ethane, propane, butanes and mixtures of these by a pressure swing adsorption process comprising the steps:
 - (a) passing said gas mixture through at least one adsorption zone containing type A zeolite having, as its exchangeable cations, about 50 to about 85% sodium ions, about 15 to about 40% potassium ions and 0 to about 10% other ions selected from Group IA ions other than sodium and potassium, Group IB, Group IIA ions, Group IIIA ions, Group IIIB ions, and lanthanide series ions, thereby adsorbing at least part of said alkene from said gas mixture and producing an alkene-depleted gas; and
 - (b) regenerating said zeolite, thereby producing an alkene-enriched gas.
2. A method according to claim 1, wherein said zeolite has as its exchangeable cations, about 55 to 80% sodium ions, about 20 to about 35% potassium ions and 0 to about 5% ions selected from said residual ions.
3. A method according to claim 1 or claim 2, wherein the exchangeable cations of said zeolite consist of sodium and potassium ions.
4. A method according to claim 1 or claim 2, wherein said residual ions are selected from copper (1) ions, lithium ions, calcium ions, magnesium ions, strontium ions, aluminium ions, and gallium ions.
5. A method according to any one of the preceding claims, wherein step (a) is carried out at a temperature of at least 50°C.
6. A method according to claim 5, wherein step (a) is carried out at a temperature in the range of about 50 to about 200°C.
7. A method according to any one of the preceding claims, wherein said alkene and said alkane contain the same number of carbon atoms.
8. A method according to any one of the preceding claims, wherein step (b) includes purging said adsorption zone with alkene-depleted gas.
9. A method according to any one of the preceding claims, further comprising purging said adsorption zone with alkene-enriched gas prior to step (b).
10. A method according to any one of the preceding claims, further comprising at least partly repressurising said adsorption zone with alkene-depleted gas after step (b).

Patentansprüche

1. Verfahren zum Trennen eines Alkens, das aus Äthen, Propen, normal-Buten oder Gemischen derselben ausgewählt ist, aus einem Gasgemisch, das das genannte Alken und ein aus Äthan, Propan, Butanen und Gemischen hiervon ausgewähltes Alkan enthält, mittels eines Druckwechsel-Adsorptionsprozesses, der die Schritte umfasst:
 - a) Hindurchleiten des Gasgemischs durch mindestens eine Adsorptionszone, die ein Typ-A-Zeolith enthält, das als austauschbare Kationen etwa 50 bis etwa 85% Natriumionen, etwa 15 bis etwa 40% Kaliumionen und 0 bis etwa 10% andere Ionen aufweist, die aus Gruppe-IA-Ionen außer Natrium und Kalium, Gruppe-IB-Ionen, Gruppe II-A-Ionen, Gruppe-III-A-Ionen, Gruppe-III-B-Ionen und Ionen der Lanthanidenreihe ausgewählt sind, wodurch mindestens ein Teil des Alkens aus dem Gasgemisch adsorbiert und ein an Alken erschöpftes Gas erzeugt wird, und
 - b) Regenerieren des Zeoliths, wodurch ein Alken-angereichertes Gas erzeugt wird.
2. Verfahren nach Anspruch 1, wobei der Zeolith als austauschbare Kationen etwa 55 bis 80% Natriumionen, etwa 20 bis etwa 35% Kaliumionen und 0 bis etwa 5% Ionen enthält, die aus den genannten restlichen Ionen ausgewählt sind.
3. Verfahren nach Anspruch 1 oder 2, wobei die austauschbaren Kationen des Zeoliths aus Natrium- und Kaliumionen bestehen.
4. Verfahren nach Anspruch 1 oder 2, wobei die genannten restlichen Ionen aus Kupfer(1)-Ionen, Lithiumionen, Kalziumionen, Magnesiumionen, Strontiumionen, Aluminiumionen und Galliumionen ausgewählt sind.
5. Verfahren nach einem der vorhergehenden Ansprüche, wobei der Schritt a) bei einer Temperatur von mindestens 50°C ausgeführt wird.
6. Verfahren nach Anspruch 5, wobei der Schritt a) bei einer Temperatur im Bereich von etwa 50 bis etwa 200°C ausgeführt wird.
7. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Alken und das Alkan die gleiche Anzahl von Kohlenstoffatomen enthalten.
8. Verfahren nach einem der vorhergehenden Ansprüche, wobei der Schritt b) das Spülen der Adsorptionszone mit an Alken erschöpftem Gas umfasst.
9. Verfahren nach einem der vorhergehenden Ansprüche, das weiter das Spülen der Adsorptionszone mit an Alken angereichertem Gas vor dem Schritt b) umfasst.
10. Verfahren nach einem der vorhergehenden Ansprüche, das weiter das mindestens teilweise Rückdruckbeaufschlagen der Adsorptionszone mit an Alken erschöpftem Gas nach dem Schritt b) umfasst.

Revendications

1. Procédé de séparation d'un alcène choisi parmi éthène, propène, butènes normaux ou mélanges de ceux-ci, d'avec un mélange de gaz comprenant ledit alcène et un alcane choisi parmi éthane, propane, butanes et mélanges de ceux-ci par un procédé d'adsorption à pression alternée, comprenant les étapes consistant à:
 - (a) faire passer ledit mélange de gaz dans au moins une zone d'adsorption contenant une zéolithe de type A possédant, en guise de cations échangeables, de 50 environ à 85 % environ d'ions sodium, de 15 environ à 40 % environ d'ions potassium et de 0 à 10 % environ d'autres ions choisis parmi les ions du Groupe IA autres que le sodium et le potassium, les ions du Groupe IB, les ions du Groupe IIA, les ions du Groupe IIIA, les ions du Groupe IIIB, et les ions de la série des lanthanides, adsorbant ainsi au moins une partie dudit alcène dudit mélange de gaz et produisant un gaz appauvri en alcène ; et
 - (b) régénérer ladite zéolithe, produisant ainsi un gaz enrichi en alcène.

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2. Procédé selon la Revendication 1, dans lequel ladite zéolithe possède, en guise de cations échangeables, de 55 environ à 80 % d'ions sodium, de 20 environ à 35 % environ d'ions potassium et de 0 à 5 % environ d'ions choisis parmi lesdits ions résiduels.
- 5 3. Procédé selon la Revendication 1 ou la Revendication 2, dans lequel les cations échangeables de ladite zéolithe sont constitués d'ions sodium et potassium.
4. Procédé selon la Revendication 1 ou la Revendication 2, dans lequel lesdits ions résiduels sont choisis parmi les ions cuivre(I), les ions lithium, les ions calcium, les ions magnésium, les ions strontium, les ions aluminium et les ions gallium.
- 10 5. Procédé selon l'une quelconque des Revendications précédentes, dans lequel l'étape (a) est réalisée à une température d'au moins 50°C.
- 15 6. Procédé selon la Revendication 5, dans lequel l'étape (a) est réalisée à une température comprise dans une plage de 50°C environ à 200°C environ.
7. Procédé selon l'une quelconque des Revendications précédentes, dans lequel ledit alcène et ledit alcane contiennent le même nombre d'atomes de carbone.
- 20 8. Procédé selon l'une quelconque des Revendications précédentes, dans lequel l'étape (b) englobe la purge de ladite zone d'adsorption avec le gaz appauvri en alcène.
9. Procédé selon l'une quelconque des Revendications précédentes, comprenant de plus la purge de ladite zone d'adsorption avec le gaz enrichi en alcène avant l'étape (b).
- 25 10. Procédé selon l'une quelconque des Revendications précédentes, comprenant de plus la remise sous pression, au moins partiellement, de ladite zone d'adsorption avec le gaz appauvri en alcène après l'étape (b).

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